基于 $CdS\text{-}SiO_2$ 纳米复合材料的过氧化物模拟酶 H_2O_2 比色传感器

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摘　要：在玻璃基板上合成 $CdS\text{-}SiO_2$ 纳米复合材料，并分别通过 X 射线衍射（XRD）和透射电子显微镜（TEM）进行表征。与自然酶辣根酶类似，$CdS\text{-}SiO_2$ 纳米复合材料可以催化 H_2O_2 氧化 3，3′，5，5′-四甲基联苯胺（TMB），产生可以通过肉眼观察到的蓝色产物，证明 $CdS\text{-}SiO_2$ 纳米复合材料具有过氧化物酶样活性。此外，$CdS\text{-}SiO_2$ 纳米复合材料在 60℃下于 HAc-NaAc 缓冲溶液（pH＝4.0）中表现出较高的活性和稳定性。另外，利用荧光探针的方法研究了催化机理，结果证明该催化机理来自于产生的羟基自由基。基于 $CdS\text{-}SiO_2$ 纳米复合材料的过氧化物酶活性，设计了一种新奇的 H_2O_2 比色传感器，检测 H_2O_2 的线性范围为 5～40 μM（R^2＝0.994），检测限为 4.2 μM。

关键词：$CdS\text{-}SiO_2$ 纳米复合材料；过氧化氢模拟酶；H_2O_2 比色传感器

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A Colorimetric H_2O_2 Sensor Based on the $CdS\text{-}SiO_2$ Nanocomposite as a Peroxidase-like Mimic

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Abstract: $CdS\text{-}SiO_2$ nanocomposites were synthesized on a glass substrate and characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively. Similar to nature enzyme, $CdS\text{-}SiO_2$ nanocomposites can catalyze the oxidation of 3,3′,5,5′-tetramethylbenzidine (TMB) in the presence of H_2O_2 to produce a blue product which can be seen by the naked eye, demonstrating that the $CdS\text{-}SiO_2$ nanocomposites possess the peroxidase-like activity. Moreover, $CdS\text{-}SiO_2$ nanocomposites exhibited a high activity and stability in HAc-NaAc buffer (pH＝4.0) at 60 ℃. Furthermore, the catalysis mechanism was studied using a probe, and proved to be from hydroxyl radicals. Based on the peroxidase-like activity of the $CdS\text{-}SiO_2$ nanocomposites, a novel colorimetric sensor was designed to detect quantitatively H_2O_2 in the range of 5 to 40 μM (R^2＝0.994) with a low detection limit of 4.2 μM.

Key words: $CdS\text{-}SiO_2$ nanocomposites; peroxidase-like mimic; colorimetric H_2O_2 sensor

Hydrogen peroxide (H_2O_2) is not only the final or the intermediate product of many biochemical reactions which are closely related with biological processes, but also an essential material used in pharmaceutical, biological, and environmental analyses[1]. For example, H_2O_2 is one of the main products of the glu-

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cose oxidase (GOx)-catalyzed reaction. Hence, the level of blood glucose can be monitored by detecting the produced H_2O_2 in the process of glucose oxidation in order to control some diseases such as diabetes mellitus. Colorimetric biosensing been applied in the various research fields, e. g. , biomedical diagnosis, environmental monitoring and food safety analysis[2-7], due to its several important advantages, such as simplicity, practicality, low cost. In this method, color changes can be distinguished by the naked eye instead of discriminated by sophisticated instrumentation and can be applied to field analysis and point-of-care diagnosis[8-10]. Several methods and strategies have been developed for this purpose, including aggregation based colorimetric immunoassay[11], lateral-flow colorimetric immunoassay[12-13] and enzyme-mediated colorimetric immunoassay[14-15]. However, the sensitivity of the methods described above is relative low because of the lack of a signal amplification step. Considering the sensitivity and selectivity of the colorimetric sensor, the use of catalysts or enzyme mimics is necessary and important. Hence, scientists have paid more attention to find peroxidase mimics instead of natural peroxidase.

Recently, with the wide development of nanoscience and technology, a lot of smart materials were found to possess intrinsic enzyme activity and shown much potential application for colorimetric biosensing on account of their unique physical or chemical properties. According to the previous reports, there are various nanomaterials have been studied, such as carbon nanotubes[16-17], nanodots[18], graphene oxide (GO) and GO composites[19], metal oxides[20], and bimetallic nanostructures[21-23], etc. These nanomaterials have been found to possess the peroxidase-like catalytic activity and could serve as promising candidates for natural enzymes in colorimetric biosensing. On the other hand, functional organic molecules modified inorganic nanomaterials have been found to possess an enhanced peroxidase mimetic activity, such as H_2TCPP-CdS nanocomposites[24], H_2TCPP-Fe_3O_4 nanocomposites[25], H_2TCPP-NiO nanoparticles[26], H_2TCPP-γ-Fe_2O_3 nanoparticles[27], H_2TCPP-Co_3O_4 nanoparticles[28] and H_2TCPP-CeO_2 nanorods[29], etc. Furthermore, some montmorillonites (MMT) supported nanocomposites, including ZnS-MMT[30] and Ag_2S-MMT [31], can catalytically oxidize peroxidase substrate TMB in the presence of H_2O_2 to produce a blue color reaction that can be easily observed by naked eye. However, to the best of our knowledge, there is no report on CdS-SiO_2 nanocomposites as a peroxidase mimic to detect H_2O_2.

Herein, CdS-SiO_2 nanocomposites were synthesized on a glass substrate by a facile method under mild conditions at room temperature, as illustrated in Fig. 1. As expected, the CdS-SiO_2 nanocomposites exhibited the intrinsic peroxidase-like activity and catalyzed the oxidation of the substrate TMB in the presence of H_2O_2 to produce a blue color reaction. Thus, the CdS-SiO_2 nanocomposites were used as peroxidase mimic to design a H_2O_2 colorimetric sensor. In addition, fluorescent results demonstrated that the peroxidase-like activity of CdS-SiO_2 nanocomposites originated from the generation of ·OH radicals. Furthermore, the colorimetric method developed here showed a much wider linear detection range than that of H_2TCPP-CdS nanocomposites as catalyst (4-14 μM) in the previous publication[24].

1 Experimental

1.1 Chemicals

Ethyl silicate ($C_8H_{20}O_4Si$), ammonia (25%, $NH_3 \cdot H_2O$), ethanol (CH_3CH_2OH), cadmium acetate ($Cd(Ac)_2 \cdot 2H_2O$), thioacetamide (C_2H_5NS), hydrogen peroxide (30%, H_2O_2), acetic acid (HAc), sodium acetate (NaAc), 3,3′,5,5′-tetramethylbiphenyl dihydrochloride (TMB·2HCl) was purchased from Solarbio (Beijing, China). All the regents above were of analytical reagent grade and used without further purification.

1.2 Characterization

Structural analysis of the synthesized samples was carried out using powder the X-ray diffraction (XRD) over the 2θ range of 10°～80°and the scan rate was 8°·min^{-1} with graphite monochromatized Cu Kα radiation (D/Max2500PC, Rigaku). The morphology of the nanocomposites was studied by using a transmission electron microscope at an accelerating voltage of 200 kV (TEM JEM-2100, JEOL, Japan). The elements composition of the CdS-SiO_2 nanocomposites was determined by energy dispersive X-ray spectroscopy (EDX, Hitachi, S4800). Ultraviolet spectra were recorded on a MAPADA UV-3200PC spectrophotometer (Shanghai, China). The photoluminescence spectras were obtained using an F-4600 FLSPECTOROPHOTOMET spectrofluorophotometer (Hitachi High-Tech Science Corporation, Tokyo, Japan).

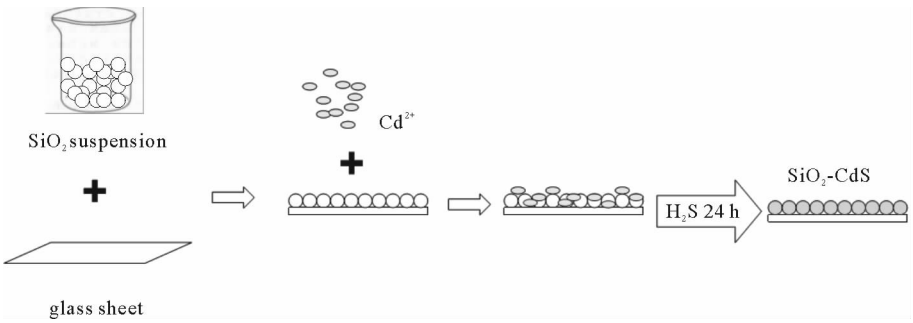


Fig. 1 The synthesis process of CdS-SiO_2

1.3 Preparation of CdS-SiO_2

As shown in Fig. 1, 20 mg as-prepared SiO_2 powder was dissolved into 2 mL deionized water and the obtained solution was dealt under ultrasonic condition for 5 min to form a homogeneous suspension. Then, the suspension was laid on a hydrophilic glass substrate. Subsequently, the glass substrate was transferred to an oven and maintained at 50℃ for 3 h. $Cd(Ac)_2 \cdot 2H_2O$ was dissolved into some deionized water to form an aqueous solution (0.4 mol/L), which was spread on the surface of the glass substrates loaded with SiO_2 nanoparticles. Simultaneously, thioacetamide was dissolved in HCl solution(0.5 mol/L). Then, the substrates and thioacetamide solution were placed into the same container for 24 h at room temperature. Finally, the faint yellow CdS-SiO_2 nanocomposites were obtained for the subsequent experiments.

1.4 Test procedure

In order to investigate the peroxidase-like catalytic activity of the CdS-SiO_2 nanocomposites, the oxidation of TMB was examined in HAc-NaAc buffer (pH=4.0) containing CdS-SiO_2 samples (2 mg/mL), H_2O_2 (25 mM) and TMB (0.1 mM) at room temperature. The tests were monitored in wavelength-scan mode after reacted for 30 min or time-course mode at 652 nm. While keeping the TMB and H_2O_2 concentration constant, kinetic analysis was performed by varying pH of the buffer (2.2-9) and temperature (20-75 ℃). Steady-state kinetic assays were carried out in HAc-NaAc buffer (pH=4.0) containing CdS-SiO_2, H_2O_2 (0.01-0.08 mM) and TMB (0.08-0.2 mM) by recording the absorption spectras at 652 nm in scanning kinetics mode.

To illuminate the catalytic mechanism of CdS-SiO_2 as a peroxidase mimic for the oxidation of TMB, a probe method was used. The detailed method is as follows, 25 mM H_2O_2, 0.5 mM terephthalic acid, and CdS-SiO_2 with different concentration(0-1.4 mg·mL^{-1}) were incubated in 1.4 mL HAc-NaAc buffer (pH=4.0) at 60 ℃ for 1 h. After that, the incubated solutions were used for the fluorometric measurement.

2 Results and discussion

2.1 Characterization of CdS-SiO_2

Fig. 2 is the XRD patterns of pure CdS, pure SiO_2 and the CdS-SiO_2 nanocomposites, respectively. As shown in Fig. 2, comparing curve b with curve a and curve c, it was easily to find that some diffraction peaks (marked with *) in curve b can be assigned to the (100), (002), (102), (110) crystal planes of the CdS nanoparticles in curve a. This result confirmed that the CdS nanoparticles was successful deposited on SiO_2 nanospheres and gave the CdS-SiO_2 nanocomposites.

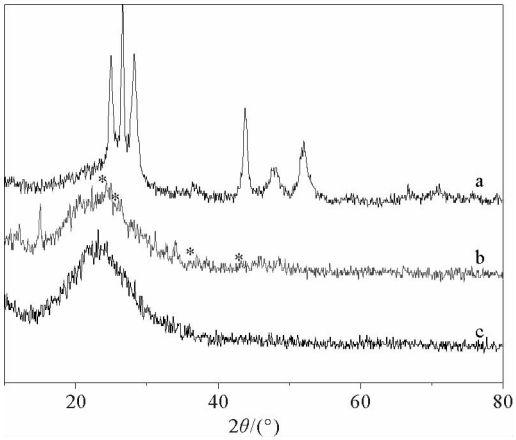


Fig. 2 XRD patterns of pure CdS nanoparticles (a), CdS-SiO_2 nanocomposites (b), and pure SiO_2 (c)

The shape, size, and structure of the as-synthesized CdS-SiO_2 nanocomposites were investigated by TEM, shown in Fig. 3. From Fig. 3, it can be seen that the nanocomposites are irregular particles with the diameter in the range of 50-150 nm.

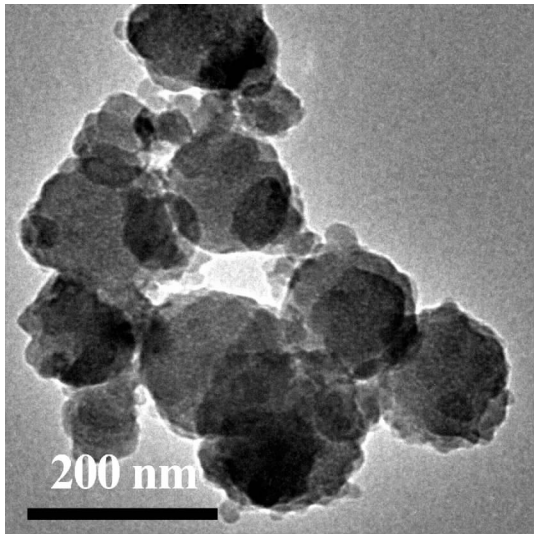


Fig. 3 TEM image of as-synthesized CdS-SiO_2

In order to confirm the successful deposition of CdS nanoparticles on the surface of SiO_2 nanospheres, the composition of the CdS-SiO_2 nanocomposites was characterized by EDX, shown in Fig. 4. The signals of elements, including Si, O, Cd and S can be found in the EDX spectrum, revealing the formation of CdS-SiO_2 nanocomposites.

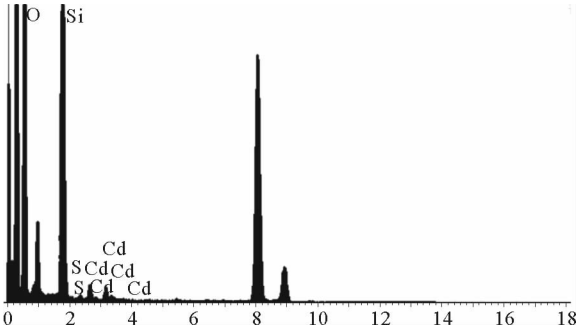


Fig. 4 EDX spectrum of CdS-SiO_2

2.2 Peroxidase activity of the CdS-SiO_2

In this study, we evaluated the catalytic activity of the CdS-SiO_2 nanocomposites using a peroxidase-like catalytic reaction involving the oxidation of TMB in the presence of H_2O_2. Control experiments suggested that CdS-SiO_2 nanocomposites demonstrate the peroxidase-like activity. It can be seen that the absorbance (652 nm) of reaction systems of CdS-SiO_2 + TMB, as well as H_2O_2 + TMB, is relative weak, shown in Fig. 5, curve a and c. Nevertheless, the absorbance (652 nm) of reaction systems of CdS-SiO_2 + H_2O_2 + TMB is stronger than that of two others described above at the identical conditions, shown in Fig. 5, curve d. Furthermore, the similar results can be also seen from the inset of corresponding photograph. In experiments, it can be found that the blue color of system d is deeper than that of system a, b and c, indicating that

both H_2O_2 and CdS-SiO_2 nanocomposites are required for the catalytic reactions. According to the previous report, as shown in Fig. 5, curve d, strong adsorption at 652 nm appeared for the CdS-SiO_2 nanocomposites + TMB + H_2O_2 system, are ascribed to the charge-transfer complexes derived from the one-electron oxidation of TMB[32], similar to the phenomena observed for the commonly used horse radish peroxidase (HRP) enzyme[33], a natural enzyme. This result revealed that CdS-SiO_2 nanocomposites could catalyze the oxidation of TMB in the presence of H_2O_2, demonstrating the peroxidase-like activity of CdS-SiO_2 nanocomposites.

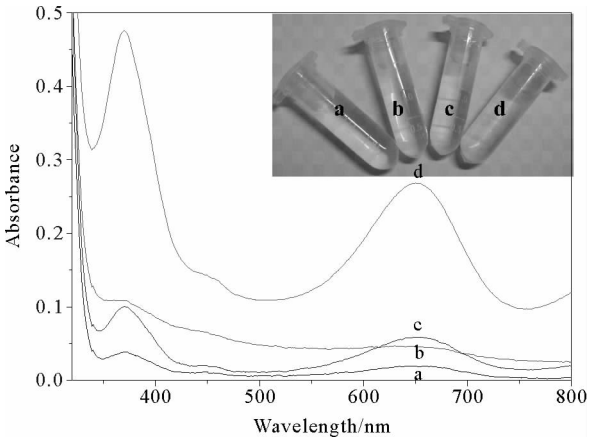


Fig. 5 UV-Vis spectra of different samples: TMB solution (a), CdS-SiO_2 + TMB (b), H_2O_2 + TMB (c), CdS-SiO_2 + H_2O_2 + TMB (d) in pH = 4.0 acetate buffer at room temperature ([TMB]: 0.1 mM; [H_2O_2]: 25 mM; [CdS-SiO_2]: 2 mg · mL^{-1}). The inset is corresponding photographs.

The peroxidase-like catalytic activity of CdS-SiO_2 was further investigated using steady-state kinetics with TMB and H_2O_2 as substrates, respectively. The details of the peroxidase-like activity of CdS-SiO_2 were fitted with the classical Michaelis-Menten model[34]. Within a certain range of TMB and H_2O_2 concentration, typical Michaelis-Menten curvescan be obtained, shown in Fig. 6 (a) and (b), respectively. The double reciprocal plots were obtained

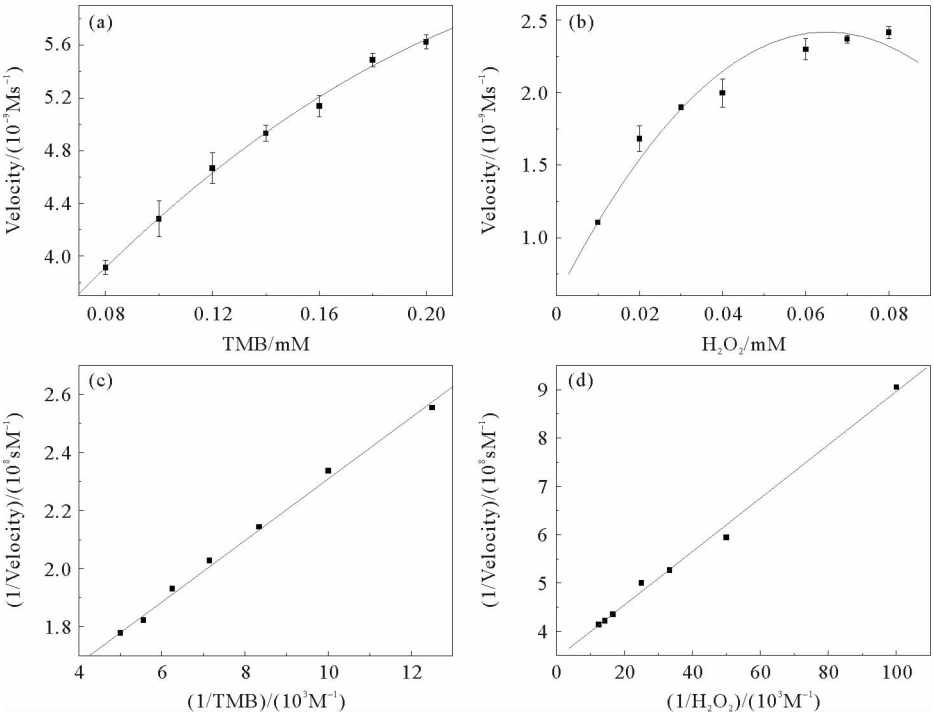


Fig. 6 Steady-state kinetic analysis using the Michaelis Menten model (a and b) and Lineweaver Burk model (c and d) for CdS-SiO_2. The concentration of TMB was 0.1 mM and H_2O_2 concentration was varied (b and d), the concentration H_2O_2 of was 25 mM and TMB concentration was varied (a and c).

according to the calculated series of the initial reaction rates by the Michaelis-Menten equation, $\nu = V_{max} \times [S]/(K_m + [S])$, where ν is the initial velocity, V_{max} is the maximal reaction velocity, $[S]$ is the concentration of the substrate and K_m is the Michaelis constant. In Fig. 6 (c) and (d), the lines were obtained by changing reciprocal initial velocity with reciprocal TMB and H_2O_2. The K_m value and V_{max} value were obtained from Lineweaver-Burk plots, shown in Table 1. As we all known, K_m is an important parameter to measure binding affinity of the enzyme to the substrate, and can be applied similarly here to study the interaction between CdS-SiO_2 nanocomposites with H_2O_2 and TMB. Smaller K_m value indicates a higher affinity between enzyme and substrate. As can be seen in Table 1, the K_m values of CdS-SiO_2 with TMB and H_2O_2 were all smaller than that of HRP, demonstrating that the CdS-SiO_2 has higher affinity to TMB and H_2O_2, compared with that of HRP[33].

Table. 1 Comparison of the apparent Michaelis-Menten constant (K_m)

Catalyst	Substrate	K_m/mM	Ref.
CdS-SiO_2	TMB	0.085	this work
CdS-SiO_2	H_2O_2	0.016	this work
H_2TCPP-CdS	TMB	0.072	[24]
H_2TCPP-CdS	H_2O_2	2.000	[24]
HRP	TMB	0.430	[33]
HRP	H_2O_2	3.700	[33]

2.3 Optimization of experimental conditions

Any catalytic reaction depends on experimental parameters to obtain the maximum activity. Efforts were made to explore the catalytic activity of CdS-SiO_2 under various conditions such as pH and temperature. The catalytic activity of CdS-SiO_2 nanocomposites was tested by varying pH values from 2.2 to 9.0 or by changing reaction temperature from 20 to 75 ℃, while keeping the other substrate constant. From the experimental results (Fig. 7 (a) and (b)), the optimized pH and temperature were found as 4.0 and 60 ℃, respectively. Therefore, 4.0 was selected as the optimum pH as well as 60 ℃ was regarded as the optimum incubated temperature.

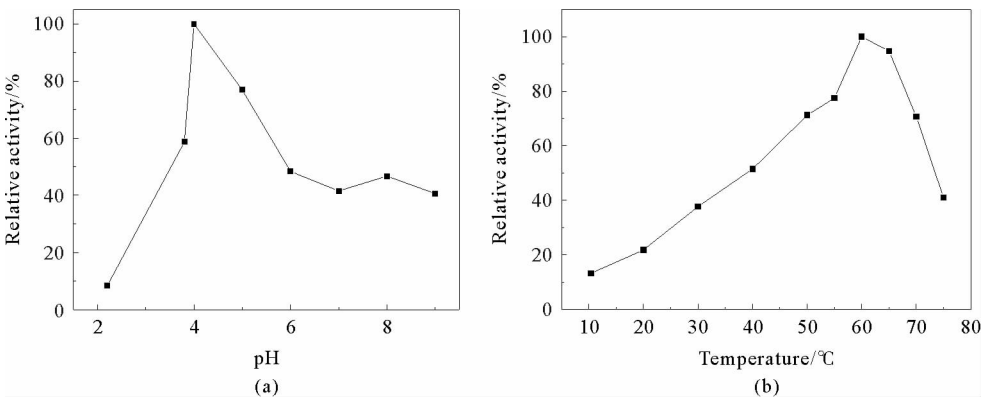


Fig. 7 The effect of physicochemical conditions on peroxidase-like activity of CdS-SiO_2: (a) pH, (b) temperature. The relative activity was defined as the ration of catalytic response at a given condition to the maximum catalytic response(The maximum point is set as 100%)

2.4 Mechanism analysis

In order to explore the catalytic mechanism of the CdS-SiO_2 nanocomposites, a fluorescent probe (terephthalic acid) was chosen to evaluate the effects of CdS-SiO_2 nanocomposites on generation of hydroxyl radicals [35]. From Fig. 8, it clearly showed that there was no fluorescence signal in the absence of H_2O_2 (curve a), while the fluorescence intensity gradually increased with the increase of the amount of the catalyst,

CdS-SiO_2 nanocomposites (curves b-g, Fig. 8). This result indicated that the catalytic activity of CdS-SiO_2 nanocomposites was attributed to the decomposition of H_2O_2 into hydroxyl radicals, as shown in Scheme 1.

2.5 Detection of H_2O_2

Because the absorbance of oxTMB is H_2O_2 concentration-dependent in the presence of the CdS-SiO_2 nanocomposites, the system described above could be used to detect H_2O_2. Fig. 9 shows a typical H_2O_2 concentration response curve under the optimal conditions. There is a good linear relationship between the absorbance at 652 nm and the concentration of H_2O_2 in the range of 5-40 μM with a detection limit of 4.2 μM. The detection method based on CdS-SiO_2 nanocomposites gave a much wider linear detection range than that of H_2TCPP-CdS NCs as catalyst (4-14 μM) in the previous publication [24].

3 Conclusions

In summary, the CdS-SiO_2 nanocomposites were found to possess intrinsic peroxidase-like activity and could catalytically oxidize the substrate TMB by H_2O_2 to produce a typical color reaction. Moreover, for the CdS-SiO_2 nanocomposites, the kinetic parameter (K_m) is significantly smaller than that of HRP indicating a stronger affinity between H_2O_2 and TMB. Furthermore, fluorescent results suggest that the nature of the peroxidase-like activity of CdS-SiO_2 nanocomposites may originate from their catalytic ability to H_2O_2 decomposition into hydroxyl radicals. In addition, based on this finding, we provide a simple, highly sensitive visual and colorimetric method for detection of quantitative detection of H_2O_2. This colorimetric assay demonstrates not only higher sensitivity but also a wider responding range to H_2O_2, suggesting promising applications in biochemical analysis and environmental monitoring.

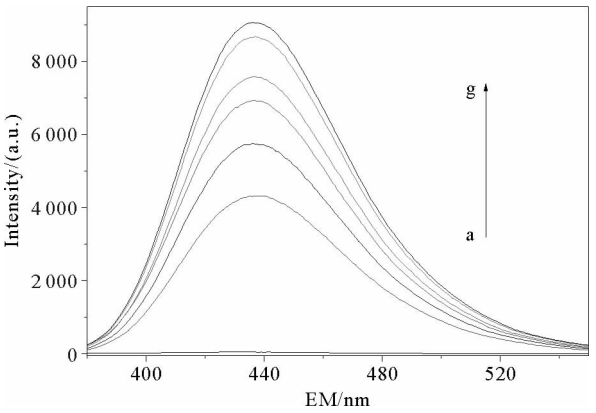
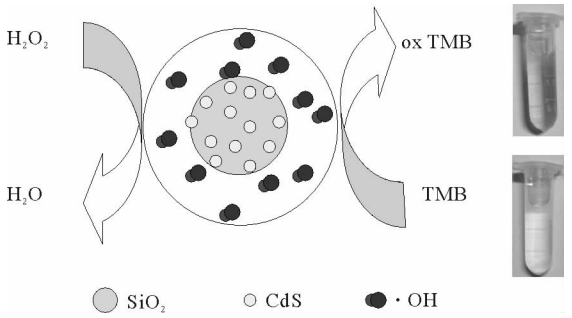


Fig. 8 Influences of the CdS-SiO_2 nanocomposites on the formation of hydroxyl radical in H_2O_2 aqueous solution with terephthalic acid as a fluorescence probe (b-g: 0-1.4 mg · mL^{-1}, line a: without H_2O_2)



Scheme 1 The catalytic mechanism of the CdS-SiO_2 nanocomposites toward the oxidation of TMB

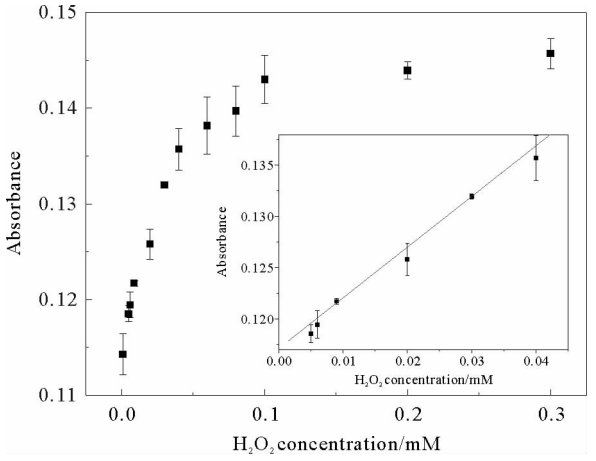


Fig. 9 A dose-response curve for H_2O_2 detection using CdS-SiO_2 nanocomposites (Inset: Plot of calibration curve for H_2O_2 concentration (5-40 μM). The error bars represent the standard deviation of the three measurements)

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